

## ORTHOPYROXENE CHRONOMETRY OF METEORITES: II. TOWARDS A GENERAL RELATION BETWEEN COOLING RATE AND CLOSURE TEMPERATURE OF CATION ORDERING AND APPLICATION TO THE STEINBACH METEORITE.

J. Ganguly<sup>1</sup>; M. Stimpfl<sup>1</sup>, and G. Molin<sup>2</sup>; <sup>1</sup>Dept of Geosciences, University of Arizona; <sup>2</sup>Dipartimento di Petrografia e Mineralogia, Università di Padova, Italy.

**Introduction:** In part I (Stimpfl et al.), we presented the thermodynamic and kinetic data governing the Fe-Mg ordering in orthopyroxene. In this paper, we present (a) a simple analytical relation among closure temperature ( $T_c$ ) of cation ordering, cooling rate at  $T_c$ , and bulk composition ( $X_{Fe}$ ) of orthopyroxene, (b) results of very precise site occupancy determination of three orthopyroxene crystals from the Steinbach (stony-iron) meteorite, and (c) the thermal history of this meteorite as reflected by cation ordering in the OPx crystals, silicate mineralogy and metal compositions. The closure temperature,  $T_c$ , is defined to be the temperature at which the observed or quenched site partitioning of Fe and Mg is in equilibrium [1].

**Analysis of the kinetic data:** As discussed in part I, analysis of the kinetic data in terms of the chemical rate theory developed by Mueller [2] makes the rate constant dependent on whether one is dealing with an ordering or a disordering process. In Mueller's model, the potential energy of the ordered state was assumed to be completely independent of the state of ordering. Modification of this theory by relaxing the latter restriction according to Ganguly [3] did not significantly reduce the dependence of the rate constant on the nature of the process. Landau theory [4] did not work any better than the Mueller theory, but unlike the latter, which yields an analytical integration of the dimensionless time lapse,  $K\Delta t$  (where  $K$  is a rate constant), associated with a given change of ordering state, use of the Landau theory leads to an expression of  $K\Delta t$  that has to be integrated numerically [5], and is therefore cumbersome without any improvement.

The results of kinetic experiments in part I (Fig. 3), and the failure of our attempts to make the rate constant independent of the nature of the process leads us to conclude that at a fixed temperature, the approach to equilibrium ordering from a disordered state is characterized by a lower potential energy maximum than that from a state which is more ordered than the equilibrium state.

**Relationship among  $T_c$ , cooling rate at  $T_c$  and bulk composition:** From analysis of the kinetic formulation, we show that for a fixed bulk composition,  $\log(dT/dt)_{T_c}$  is a linear function of

$\log(T_c)$ , where  $(dT/dt)_{T_c}$  is the cooling rate at  $T_c$ . In principle, the cooling rate retrieved from any temperature sensitive property is strictly valid only near its closure temperature. Using the equilibrium and kinetic data presented in part I, we calculated the  $\log(dT/dt)_{T_c}$  vs.  $\log(T_c)$  for fixed bulk compositions of orthopyroxene. Results for  $F_s = 0.25$  is illustrated in Fig. 1. The relationship does not, however, change significantly for  $F_s = 0.15$ . There is a small compositional dependence for  $F_s > 0.25$ , which will be incorporated into a general expression of  $dT/dt$  as  $f(T_c, X_{Fe})$  after the kinetic data are refined. The two curves correspond to the two different expressions of the rate constant  $K^+$  derived from the ordering and disordering experiments. The cooling was assumed to follow a  $T$ - $t$  path given by  $1/T = 1/T_0 + \eta t$ , where  $\eta$  is a cooling time constant, so that  $dT/dt = -\eta T^2$ . The  $T$ - $t$  path can be extrapolated by recovering the value of  $\eta$  from  $(dT/dt)_{T_c}$  which is illustrated in Fig. 1.

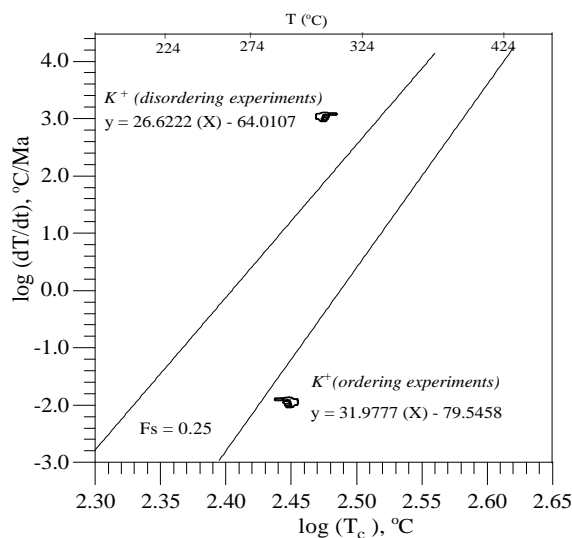


Fig. 1: Relationship between the  $T_c$  of cation ordering and the cooling rate at  $T_c$  for  $X_{Fe(OPx)}=0.15-0.25$ , using rate constant ( $K^+$ ) derived from ordering and disordering experiments. The latter provides an upper limit on cooling rate at a given  $T_c$ .

Since cooling leads to ordering, we should use the relation between cooling rate and  $T_c$  derived on the basis of the rate constant ( $K^+$ )

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retrieved from the ordering experiments. However, the data on ordering experiments, although internally consistent, are still too few to lead to a precise Arrhenian relation (part I, Fig. 3). Thus, we also showed the cooling rate vs.  $T_C$  derived from  $K^+$  retrieved from disordering data, which places an upper bound on the  $(dT/dt)_{T_C}$ , since  $K^+$ (disordering expt)  $> K^+$ (ordering expt).

## Thermal history of Steinbach meteorite:

Steinbach is a stony-iron meteorite, in which the silicate portion consists of ortho-bronzite, proto-bronzite and trydimite, but no olivine. Reid et al. [6] inferred an equilibration temperature of 1200 °C and  $fO_2 = 10^{-12}$  bars (~WI buffer) for this assemblage. They concluded that the silicate mineralogy indicates a very rapid cooling rate (comparable to that of terrestrial volcanic rock) the temperature range 1200-700 °C, which is in contrast to the very slow cooling rate, of the order of 10 °C/Ma, through 700-500 °C determined from the taenite border composition according to the method of Short and Goldstein [7].

We determined the site occupancies of three orthopyroxene crystals separated the Steinbach meteorite (Table 1) with a precision of  $\leq 0.002$  (total of 1 cation per site) according to the method discussed in part I.

Table 1: Site occupancies and closure temperature ( $T_C$ ) of Fe-Mg ordering of orthopyroxene crystals from the Steinbach meteorites.

| Crystal          | 1-ST77     | 2-ST71     | 3-ST76     |
|------------------|------------|------------|------------|
| <b>M1 site</b>   |            |            |            |
| Mg               | .9697 (16) | .9675 (19) | .9746 (20) |
| Fe*              | .0152      | .0162      | .0146      |
| Al               | .0000      | .0000      | .0000      |
| Cr <sup>3+</sup> | .0151      | .0158      | .0105      |
| Ti <sup>4+</sup> | .0000      | .00005     | .00003     |
| <b>M2 site</b>   |            |            |            |
| Mg               | .6805 (19) | .6749 (18) | .6879 (18) |
| Fe*              | .3054      | .3051      | .3015      |
| Ca               | .0140      | .0200      | .0106      |
| Na               | .0000      | .0000      | .0000      |
|                  |            |            |            |
| $\ln k_D$        | -3.3553    | -3.2968    | -3.3784    |
| $T_C$ (°C)       | 452        | 463        | 448        |

Using the relation between intracrystalline distribution coefficient ( $k_D$ ) and  $T$  presented

therein, these data yield  $T_C$  between 447 and 462 °C (mean 454 °C). Comparison of these  $T_C$  values with Fig. 1 clearly show that the cooling rate of the orthopyroxenes must be  $> 1$  °C/100 at  $\sim 450$  °C, which is again in sharp contrast to the very slow metallographic cooling rate at 700-500 °C. Thus, the Steinbach meteorite had either experienced a complex thermal history (very rapid cooling at 1200-700 °C and 700-500 °C separated by very slow cooling at 700-500 °C) or the metal and silicate portions were derived from sources that had experienced slow and rapid cooling, respectively.

We also note that the Steinbach silicates show no evidence of shock effects [6], which rules out a model of resetting of the Fe-Mg ordering of orthopyroxene subsequent to slow cooling reflected by the metal texture and composition.

**References:** [1] Ganguly, J. (1982), *Adv Phys Geochem* 2, 58; [2] Mueller, R.F. (1967) *J Phys Chem Solids*, 28, 2239. [3] Ganguly (1986), *J Phys Chem Solids*, 47, 417; [4] Salje, E.K.H. and Kroll, H. (1991) *J Phys Chem Solids* (1991), 17; [5] Redfern, S.A.T. et al. (1996), *Nature*, 381, 407; [6] Reid et al. (1974), *EPSL*, 22, 67; [7] Short and Goldstein (1967), *Science*, 156, 59.